

Anodic Oxidation of Benzaldehyde Phenyl Hydrazones in the Presence of Benzonitrile — Mechanism of Triazole Formation

Bernd Speiser

Universität Tübingen, Institut für Organische Chemie
Auf der Morgenstelle 18
D – 72076 Tübingen
Germany

Wolfgang Märkle

Universität Tübingen, Institut für Organische Chemie
Auf der Morgenstelle 18
D – 72076 Tübingen
Germany

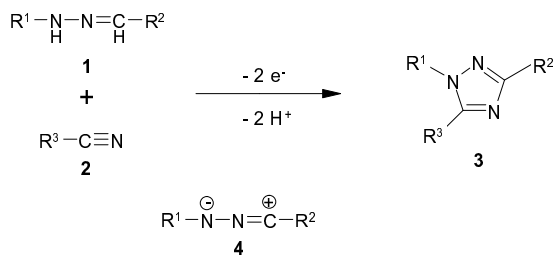
Katrin Probst

Universität Tübingen, Institut für Organische Chemie
Auf der Morgenstelle 18
D – 72076 Tübingen
Germany

Günther Jung

Universität Tübingen, Institut für Organische Chemie
Auf der Morgenstelle 18
D – 72076 Tübingen
Germany

Electrochemical procedures are advantageously used in the synthesis of various classes of chemical compounds, e.g. heterocycles [1]. Detailed knowledge of the reaction product's formation mechanism is crucial for the optimization of the overall synthesis. Product studies and electroanalytical experiments are usually combined in order to elucidate the pathways of the reaction. Here, we present results for the formation of 1,2,4-triazoles **3** from benzaldehyde phenyl hydrazones **1** (R^1 , R^2 : p-substituted phenyl) oxidized in dichloromethane/0.1 M NBu_4PF_6 at Pt electrodes in the presence of benzonitrile **2** (R^3 = phenyl).



A synthetic strategy to form 1,2,4-triazoles is the 1,3-dipolar cycloaddition of nitrilimines **4** to nitriles in a purely chemical process [2]. The formation of **3** via electrogenerated **4** was proposed by Jugelt [3] and the intermediate **4** was also postulated in an analogous anodic reaction [4]. However, no direct, e.g. spectroscopic, evidence for electrogeneration of **4** was provided in the earlier work.

The formation of **4** from hydrazone **1** was explained by an ECEC type sequence with initial generation of a radical cation $\mathbf{1}^{\bullet+}$ and the subsequent deprotonation of this species coupled to further oxidation and another deprotonation. There are, however, alternative pathways to synthesize **3** from **1** and **2** through oxidation. One of these is the direct attack of **2** on $\mathbf{1}^{\bullet+}$. Addition of a base should favour the formation of **4**. However, experiments in the presence of pyridine or 2,6-lutidine in some 10-fold excess over **1** showed that *no* **3** is formed. Although pyridine is known to react with nitrilimines (2-substitution) [5] the reactivity of 2,6-lutidine is expected to be low due to the blocking of the reactive positions. Thus, we exclude the nitrilimine pathway for triazole formation.

Under non-basic conditions, however, **3** is generated and was detected by HPLC-MS coupling and NMR experiments.

Cyclic voltammograms of **1** ($R_1 = R_3$ = phenyl, R_2 = p- CH_3O -phenyl) at various scan rates and concentrations in the absence and presence of $\text{C}_6\text{H}_5\text{CN}$ were recorded and digitally simulated. Several side reactions had to be included into the mechanism in order to successfully model the experimental curves, notably self-protonation of the neutral starting hydrazone by $\mathbf{1}^{\bullet+}$ (even without benzonitrile) and dimerization of $\mathbf{1}^{\bullet+}$. The simulation of results with $\text{C}_6\text{H}_5\text{CN}$ support a mechanism with direct attack of benzonitrile on $\mathbf{1}^{\bullet+}$. Quantitative comparisons of the computed and the experimental curves for all experimental conditions provide numerical values for the rate constants of the various steps (chemical and electrochemical) as well as for the formal potential of the primary oxidation step $\mathbf{1} \rightleftharpoons \mathbf{1}^{\bullet+} + \text{e}^-$.

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Presenting Author:

Speiser, Bernd

Universität Tübingen, Institut für
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Complete Author List:

Bernd Speiser

Universität Tübingen, Institut für
Organische Chemie

Auf der Morgenstelle 18

D – 72076 Tübingen

Germany

Phone: +49-7071-297-6205

Fax: +49-7071-295518

E-Mail: bernd.speiser@uni-tuebingen.de

Wolfgang Märkle

Universität Tübingen, Institut für
Organische Chemie

Auf der Morgenstelle 18

D – 72076 Tübingen

Germany

Phone: +49-7071-297-6242

Katrin Probst

Universität Tübingen, Institut für
Organische Chemie

Auf der Morgenstelle 18

D – 72076 Tübingen

Germany

Phone: +49-7071-297-8714

Günther Jung

Universität Tübingen, Institut für
Organische Chemie

Auf der Morgenstelle 18

D – 72076 Tübingen

Germany

Phone: +49-7071-297-6925

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